PREBIOTIC REACTIONS IN THE BUBBLE THAT WAS FORMED IN CARBONATED WATER BY IRON ATOMS

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Abstract
The bubbles are observed by mixing of fine powder of iron into carbonated water. Large bubble formed from the small bubbles by unification. It carries the fine powder of iron to the surface of water. The bubble at surface of water will burst, and the debris will sink to bottom. Robustness of the bubble increases after repetition of creation and destruction. These bubbles are generated after a few hours from the mixing, but those are not generated after a week. The measured value of pH (acidity) indicates that the bubbles are suitable for the existence of hydrogen-carbonate (HCO3-). It is considered that the membrane of the bubble is formed by intermolecular binding force between HCO3- and Fe2+. The membrane is able to accumulate molecules selectively in order to form an organization of molecules. It might have been functioned as a platform of chemical evolution, because the ultraviolet light in the early earth is able to provide the energy to cause chemical reactions.

(Keywords) carbonated water, intermolecular interaction, bubble, membrane, ferrous bicarbonate, metabolism, chemical evolution, BIF

1. Introduction

Observations on the bubbles made from the carbonated water with fine powder of iron are reported in this article. Although the bubble is observable, it is difficult to decide the structure. The membrane of a bubble is formed by intermolecular bonding force among ions at the interface of the liquid. The system of molecules is able to accumulate molecules. The intermolecular interaction would give a step for chemical reactions. The bubble could be repaired by mechanism of the production. It is a self-sustained organization of molecules. It was considered that the bubble is a prime candidate for the origin of life.

Many scientists have been interested in the origin of life [1]. After proposal on the origin of life by A. I. Oparin, many models have been proposed [2,3]. But, the detailed mechanism to form the organization of intermolecular bonding force has not been discussed.

Z. Borowska & D. Mauzerall reported the formation of organic molecule caused by reduction of carbon dioxide ($CO_{2(aq)}$) under the condition of irradiating aqueous ferrous ion (Fe^{2+}) at neutral pH with near-UV light (306-390 nm) [4,5]. However, there is no report of study on the bubble that was formed by means of intermolecular bond among polyatomic ions of HCO_3^-.

S. Karasawa (2010) had reported that bubbles are made from the carbonated water in which fine powder of iron is dissolved [6]. But it had been written without consideration of intermolecular bonding effects. In this paper, the study on the organization of intermolecular bonding basing on the observation on the bubbles that is formed in the carbonated water by powder of iron is reported.

2. Observations of bubbles that are formed in carbonated water by mixing of iron powder

2.1 Experimental procedures

After mixing fine powder of iron into the carbonated water, the glass container was sealed in order to hold the carbon oxide gas in the bottle. The observations of bubbles were carried out from the outside of the sealed glass container. Most of photographs were taken by digital camera PENTAX Optio W 90. The close-up photos were taken in microscope mode with LED 3 point lighting.

The materials used for observations were prepared as follows. The carbonated water was provided by Japanese Consumers' Co-operative Union as pure carbonated water but it included only very small amount (13 ppm) of sodium. Nearly the same results were observed by using the carbonated water that was produced from tap water mixed with dry ice.

The iron powder [the grain size is about 50 microns (meshed #300), and the purity is Fe 90% or more.] was produced by Kyowa Pure Chemicals Industry Co. (We can get by mail-order of internet.) Even by addition of steel wool, similar floating materials were observed on surface of the carbonated water made by tap water mixed with dry ice (CO_2) [6].

The purity of materials for the experiment is required to ensure experimental reproducibility. But every material includes impurities in fact. The repeatability of this description will be guaranteed by the common characteristics obtained in many different experiments. The other several of results for the evidences are able to be obtained at the website of [7].

2.2 The adhering of iron particles to a block of dry ice ($CO_{2(s)}$) in liquid water

By mixing fine powder of iron into the carbonated water, we can observe the phenomena shown in Fig.1.

A block of dry ice ($CO_{2(s)}$) in water collects the fine powder of iron. There is Brownian motion of powder of iron. Thermal motion of cluster of water is able to change the position of very fine powder of iron in water. The adhering indicates the existence of a long-range force between carbon dioxide and powder of iron in the water. Generally speaking, every atom has the adaptability to its circumstance. The metabolism is supported by the long-range force and thermal motion.

The most of intermolecular bonding structure will be decomposed by the thermal motion of molecule. But, the thermal motion is suppressed in some interconnected molecules. So, decomposition of intermolecular bonding material will be suppressed by the interconnection. The intermolecular bonding material will be changed into compound by the energy given from outer world such as the irradiation of ultra violet light.

Fig.1 Fine powder of iron (Fe) adhered to the block of dry ice (CO_2) in carbonated water. The right bottle includes the iron powder of meshed #300. The left bottle includes the iron powder of meshed #200.

2.3 The bubble that was formed in carbonated water by iron particles

The membrane of bubble that includes with particles is produced by mixing iron powders in carbonated water as shown in Fig.2.

At first, molecules of carbon dioxide in the carbonated water are gathered by adhering at the surface of iron (Fe). After that, small bubbles are generated at surface of the iron powder. The fine particles of iron are incorporated in the membrane of bubble. After a while, the small bubbles become big by coalescing with each other. The big bubble is able to rise with fine particle of iron to surface of water.

The floating material at the surface is a thin plane. It escapes from a spoon of stainless steel. It is explained that the floating material includes Fe^{2+} ions.

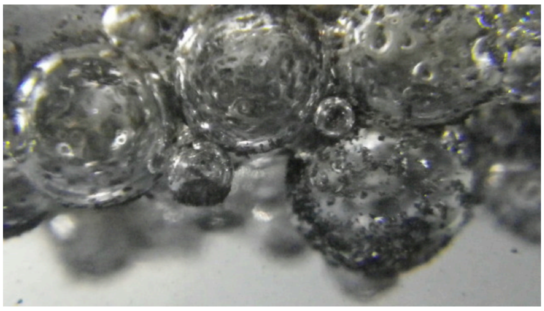

Fig.2 Bubbles that were generated in the carbonated water (saturated solution 75 cc) that had been mixed with fine powder (#300) of iron (5 g). This photograph was taken after 75 hours from mixing.

2.4 A primitive metabolism that is observed in bubble

Intermolecular bond in the membrane of bubble is different from that of inside of liquid water. The intermolecular binding force at the interface is emphasized by regular alignment of molecules. In a bubble, the molecules of membrane form a cage structure of molecules.

The shape of bubble responds to external and internal changes. The membrane of a bubble is flexible. The flexibility is caused by weak intermolecular binding force. Although the bubble is robust against shaking the water, it is easily broken by stopping the shaking [8]. The process of repair is the same to the production. The long life of bubble is yielded under the condition of production. The continuous renewing will achieve the long life. This phenomenon indicates the origin of metabolism.

The metabolism is carried out by the adaptability of electronic structure of atom and together with the intermolecular force among the neighboring atoms. Here, neighboring atoms will be exchanged by thermal motion of molecules in the substances. The organization of molecules will be changed by the result of reaction. The renewed environment produces renewed products.

3. Analyses on the substance of the bubble

3.1 Observations of dried bubbles

It is difficult to analyze the state of bubble. The sample to be analyzed was dried. We can see the dried bubbles at the upper wall of the glass bottle as shown in Fig.3. We can recognize two types of

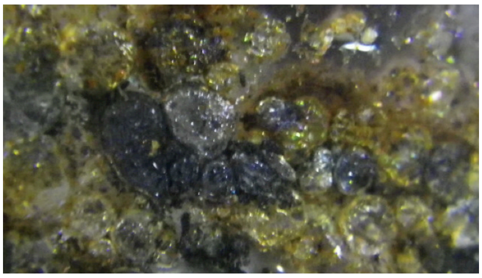

Fig.3 The dried bubbles that had been adhered to the wall of the glass.

Fig. 4 (a) Dried floating materials. (b) Membrane on a wall. Fig.4 (a) is the photo on the dried floating materials made from carbonated water and steel wool. Fig.4 (b) is the photo on the membrane that was formed by adhering to the wall of the glass in 90 cc of carbonated water mixed with 5 g of #300 iron powders.

substances in Fig.3. One is black particle made of iron powder. The other is yellow membrane of transparency.

Fig.4 (a) is photograph of dried specimen on a laboratory dish. On the other hand, a structural color is observed on glass wall. The membrane has been formed adhering to the glass wall. Fig.4 (b) was photographed after 5 months from mixing iron and carbonated water. The sample (b) was irradiated by ultraviolet light during a few days at beginning of the period of 5 months.

3.2 Inspections by Fourier Transform Infrared Spectroscopy (FT-IR)

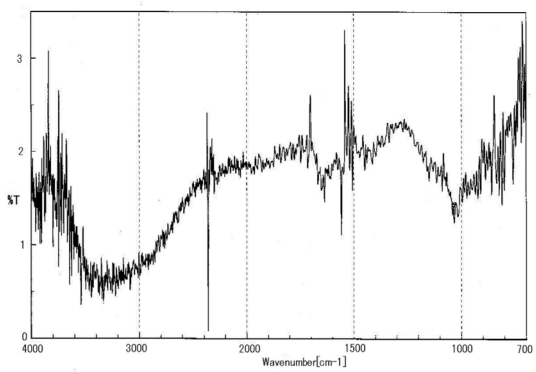

Fig.5 An example of FT-IR data on the dried membrane of bubble.

FT-IR on the dried membrane of bubble was measured [6]. A new example of data is shown in Fig.5. But, it is difficult to clarify the meaning of the peak from this data, because the confirmed referable data on such materials do not exist. At this point, it is difficult to decide the weak structure of the membrane of bubble by FT-IR. The accumulation of many kinds of data will contribute to decide the structure in the future.

3.3 Inspections by energy dispersive X-ray spectrometry of scanning electron microscopy

The dried membrane of the bubble was inspected by energy dispersive X-ray spectrometry (EDS) of scanning electron microscopy [6]. The substance contains atoms of carbon (C), oxygen (O) and iron (Fe). Here, the hydrogen (H) does not appear in this EDS analysis. As the result of existence of iron particle, the ratio among these elements differs by the position of analysis.

A large peak of oxygen atom (O) is detected in case of the sample of which surface is covered with Au coating (Fig.6). But in the sample that did not coating of Au, the amount of oxygen remarkably decreases. The facts indicate that the membrane will be contained with many H_2O molecules.

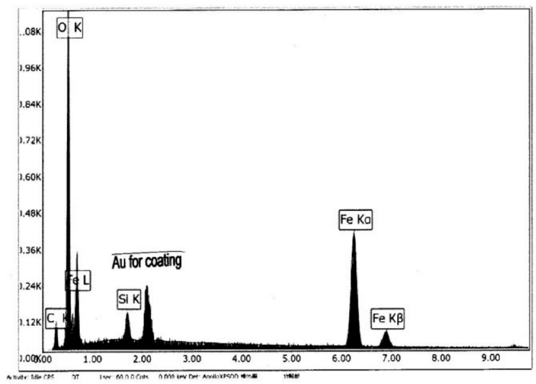

Fig.6 In case of the sample that is covered with Au coating, a large amount of oxygen is detected by X-ray spectrometry (EDS) of a scanning electron microscopy (SEM).

4. **The mechanism that forms bubbles in carbonated water by iron atom**

4.1 Changes of pH value on the water (75 cc) under the atmosphere of 1 atm of 100% CO_2

When CO_2 gas dissolves in water, 3 different forms can occur i.e. $H_2CO_{3(aq)}$, $HCO_3^-{}_{(aq)}$ and $CO_3^{2-}{}_{(aq)}$ (p.107, Fig.19 [9]). Activities of those species in the carbonated system are given by Drever (1988). Major species in the carbonated water is divided into following 3 regions (p.224 [10]).

$$\underline{H_2CO_3} < pH=6.35 < \underline{HCO_3^-} < pH=10.33 < \underline{CO_3^{2-}}$$

The value of electrolytic dissociation constant of is small. So, the most of dissolved carbon dioxides are the form of molecules. The reactions are as follows.

$$CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_{3(aq)}; \quad K_{CO2} = 10^{-1.47} \qquad (1)$$
$$H_2CO_{3(aq)} \Leftrightarrow HCO_3^-{}_{(aq)} + H^+{}_{(aq)}; \quad K_{a1} = 10^{-6.35} \qquad (2)$$
$$HCO_3^-{}_{(aq)} \Leftrightarrow CO_3^{2-}{}_{(aq)} + H^+{}_{(aq)}; \quad K_{a2} = 10^{-10.33} \qquad (3)$$

The values of equilibrium constants for the carbonate system are for fresh water at 25°C from (p.221 [10]). The reactions Eq.(2) and Eq.(3) produce hydrogen ion ($H^+{}_{(aq)}$). An amount of the hydrogen ion in natural water mainly depends on the reaction of Eq.(2).

The value of pH on the water is changed (Fig.7), when the atmosphere on surface of water is 100% CO_2, and the pressure is 1 atm. The volume of water is 75 cc in a vessel of 100 cc with cross section of 30 cm^2.

The available hydrogen ions are increased by dissolved carbon dioxides. The increase of hydrogen ion will lower the value of pH. But, the hydrogen ion in aqueous solution becomes associated with an oxygen atom in the water.

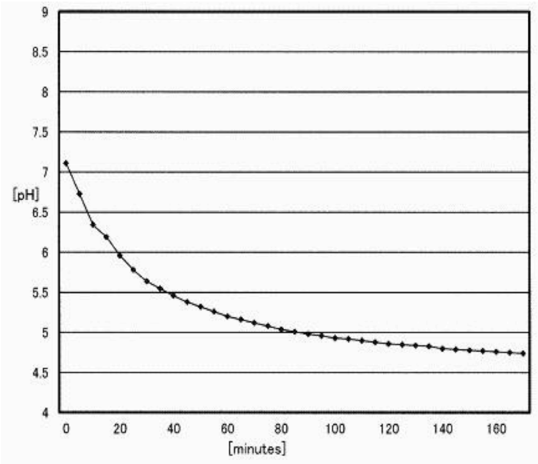

Fig.7 Changes of pH value on the water (75 cc) under the atmosphere of 1 atm of 100% CO_2.

4.2 Changes of alkalinity of the carbonated water by mixing of fine powder of iron

Fine powder of iron dissolves slowly in the carbonated water. The hydrogen ions in carbonated water are decreased by the iron ion. The measured values of pH increase along the time progress as shown in Fig.8.

These results are the evidences of indication that HCO_3^- is effects to form the inorganic bubble.

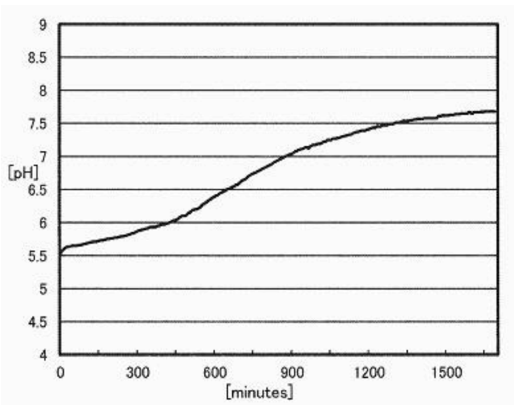

Fig.8 Changes of pH value on carbonated water (75 cc) after mixed with powder of iron (#300, 5 g)

4.3 The model that produces bubbles in the carbonated water by mixing of powder of iron

When Fe atom connects with $OH^-_{(aq)}$, the connection forms a unit of $Fe(OH)_2$. In this case, the molecule of CO_2 will gather and it is able to produce gas of CO_2 as illustrated in Fig.9.

4.4 The model that produces membrane in the carbonated water by mixing of powder of iron

Another units of planer structure of $Fe(HCO_3)_{2(aq)}$ is illustrated in Fig.10. The positioning of atoms in Fig.10 is nearly the same to Fig.9. There are intermolecular bonds between an ion of iron (Fe^{2+}) and polyatomic ions of $HCO_3^-{}_{(aq)}$ (Fig.10).

Each carbonic acid (CO_3^{2-}) in liquid state takes a

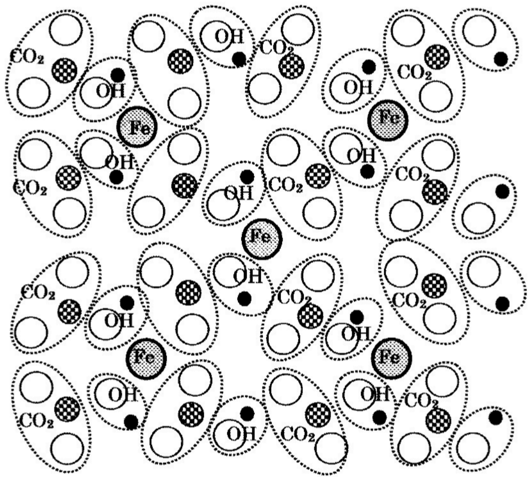

Fig.9 The molecular model of $Fe(HCO_3)_{2(aq)}$ that indicates the forming of $CO_{2(g)}$ by mixing fine powder of iron into the carbonated water.

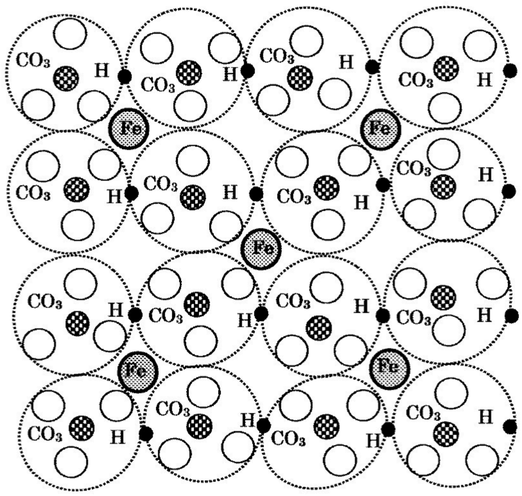

Fig.10 A molecular model of membrane by $Fe(HCO_3)_{2(aq)}$. The positioning of atoms in Fig.10 is nearly the same to Fig.9. The polyatomic ion of the $HCO_3^-{}_{(aq)}$ that makes hydrogen bonds attaches to an iron atom.

plane triangle structure of 3 oxygen atoms equivalent joined around one carbon atom. The paralleling line of hydrogen bond of carbonic acid ions HCO_3^- is connected by iron (Fe^{2+}) atom two-dimensionally.

This structure is able to explain the mechanism of proton motive force, because the movement of hydrogen bond accompanies with that of the deformation.

Generally speaking, the iron atom is able to form a complex. It is organized by d-electron of the iron ion. The membrane of $Fe(HCO_3)$ is able to accumulate molecules selectively in order to form an organization of molecules.

5. Effects of bubbles on geochemistry in the Early Earth

5.1 The oldest microbial mats and BIF

M. M. Tice & D. R. Lowe reported the oldest microbial mats and banded iron formations (BIF) those had formed at 3.416 billion years ago in Buck Reef Chert, South Africa [11]. The BIF is iron-rich, but the other metal is low concentration in it. The BIF at South Africa includes iron carbonate ($FeCO_3$). $FeCO_3$ was produced in the alkali state of carbonated water that was caused by means of addition of iron ion, i.e., it was produced by dehydration accompanying with supply of iron as follows.

$$Fe^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)} \Leftrightarrow Fe(HCO_3)_2 \quad (4)$$
$$Fe(HCO_3)_2 \Leftrightarrow Fe(OH)_2 + 2CO_{2(g)} \quad (5)$$
$$Fe(HCO_3)_2 + Fe(OH)_2 \Leftrightarrow 2FeCO_{3(s)} + 2H_2O_{(aq)} \quad (6)$$

There are reports on UV driven photo-oxidation of ferrous ions for banded iron formation (BIF) ([12-14]). The photo-oxidation of iron atom may generate formaldehyde (HCHO) [5] and molecular hydrogen (H_2) [15]. These products of the photoreaction would be able to make membrane of the robust bubble.

Isotope of ^{12}C is taken easily in the bubble compared with ^{13}C, because the thermal motion of atom is required for the photoreaction. The effect of thermal motion is also functioned at the photosynthesis that produces organic molecules.

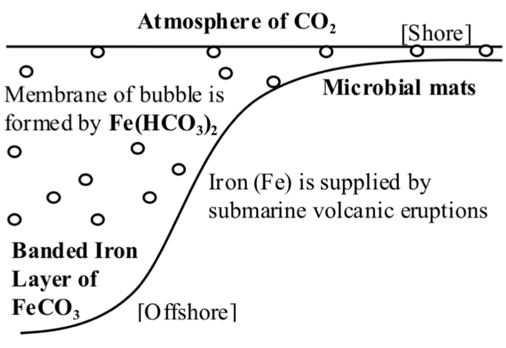

Fig.11 An illustration on the formation of microbial mats at 3.42 billion years ago in Buck Reef Chart in South Africa [11].

Fig.11 is an illustration of the above mentioned mechanism of BIF and microbial mats.

5.2 The scenario of the bubble related with the formation of oldest organic carbon

The facilities for production and the products are present at the same time. So, the production of the oldest organic carbon from inorganic matter is likely to occur simultaneously with the birth of organism. However, the production of the oldest organic molecule by means of the photosynthesis is difficult, because a complicate system of organic molecules is necessary for the photosynthesis.

The following story can be postulated. At about 3.5 billion years ago, temperature of seawater became mild from hot temperature. The carbon dioxide in the atmosphere was dissolved in the water at lower temperature. At the same period, iron particles were emitted by the volcanic eruptions.

The floating material was produced from carbonated water with iron. It was oxidized by the energy that came from outer world. And the iron oxide was deposited at the bottom of sea. That is the formation of BIF.

On the other hand, neighboring atoms in carbonated water with iron are able to exchange by thermal motion [16]. There is the adaptability of substance that is caused by the electronic structure. Some organic molecules were produced from the floating substance of intermolecular bonds by the energy that comes from outer world such as ultraviolet ray. The molecules will be evolved through the repetition of production and destruction. That would be chemical evolution.

The carbon isotope of ^{12}C in liquidity state of substance can be accumulated in the substances floated in the early sea, because the motion of ^{12}C is more active than ^{13}C .

The structure that is formed by $Fe(HCO_3)_{2(aq)}$ is able to realize a proton driving force. That is, the weak intermolecular bond by the proton is able to move together with a deformation of the structure. Since process of repair is the similar to the production, the bubble is self-sustained system. The bubble is an autonomous system with open-ended evolutionary capacities. It may satisfy the definition of life [17], "Life is a self-sustained chemical system capable of undergoing Darwinian evolution" (Joyce, 1994).

6. Conclusions

The robust bubbles covered with particle of irons were generated in the carbonated water after several hours from mixing of powder of iron. The membrane of bubble is formed by a weak intermolecular bond. How to decide the delicate molecular structure of intermolecular bonding state is remained for the future work.

Although we cannot directly analyze those bubbles, we can estimate the model of consistent structure from many evidences. That is, each Fe^{2+} is surrounded by 4 pieces of HCO_3^- ions. There are hydrogen bonds between HCO_3^- ions. So, $Fe(HCO_3)_2$ forms a planer structure, and it forms membrane of the bubble. Moreover, the structure of $Fe(HCO_3)_{2(aq)}$ has advantages to induce chemical reactions. It is able to operate the primitive metabolism.

The bubble can be functioned as a platform of prebiotic reaction. The intermolecular reactions at long period in the early earth had effected to the substances on the earth. It is possible to contribute to explain about the formation of oldest organic carbon and BIF.

The proposing model on the bubble of weak intermolecular bonds in liquid water between the iron atom and polyatomic ions of HCO_3^- is a start for the molecular study of the chemical evolution.

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